

# Easy orientation of diblock copolymers on self-assembled monolayers using UV irradiation

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## Abstract

A simple method based on UV/ozone treatment is proposed to control the surface energy of dense grafted silane layers for orientating block copolymer mesophases. Our method allows one to tune the surface energy down to a fraction of a mN/m. We show that related to the surface, perpendicular orientation of a lamellar phase of a PS-PMMA diblock copolymer (neutral surface) is obtained for a critical surface energy of 23.9-25.7 mN/m. Perpendicular cylinders are obtained for 24.6mN/m and parallel cylinders for 26.8 mN/m.

The control of the surface energy of self-assembled monolayers (SAMs) for orientating diblock copolymer mesophases has been achieved using different methods. The goal is usually to obtain a neutral surface, that is a surface exhibiting similar interfacial energies with both blocks of the copolymer in order to promote perpendicular orientation. Historically, the first method to be used was to spin coat random copolymers made of the same monomers on the substrate,<sup>1</sup> as different surface energies can be achieved by varying the ratios of monomers in synthesis. Further, a major improvement was to modify the random copolymer at one end with a chemical group which could be grafted on the surface in order to prevent the random

copolymer to dewet or diffuse in the block copolymer.<sup>2,3</sup> Besides of this surface specific chemistry, cross-linking on the random copolymer has also recently been used to increase the film stability.<sup>4</sup> More recently, the thickness dependence of the orientation has been investigated<sup>5</sup> and it has been shown that the formation of perpendicular domains on a random copolymer brush needs to be viewed in terms of the equilibration of the block copolymer and the random copolymer in the presence of each other and not simply in terms of interfacial energy.<sup>6</sup>

A different strategy has been to use self-assembled monolayers (SAM) like silanes. However, though it has been shown that 3-(*p*-methoxyphenyl)propyltrichlorosilane could provide neutral surfaces for PS-PMMA (polystyrene-poly(methyl methacrylate)) on a silicon wafer,<sup>7</sup> such monolayers usually don't have the right surface energy and different methods have been used in order to control this energy. It has for example been shown that incomplete silane monolayers could also be used.<sup>8</sup> Whereas this method is extremely versatile, it leads to a necessarily heterogeneous film which might prevent control at very small scales. Another possibility is irradiation of SAMs with synchrotron soft X-rays,<sup>9,10</sup> or treatment with CO<sub>2</sub> plasma.<sup>11</sup> Oxidation through ultraviolet (UV) radiation has also been recently used to produce wettability gradients.<sup>12</sup> In this paper we show that UV irradiation indeed provides a versatile tool to precisely tune the surface energy of a SAM. We show in particular that the orientation of PS-PMMA lamellar and cylinder phases can be controlled using this method.

Si wafers (p-type, boron doped, 250  $\mu\text{m}$  thick) were first cleaned by sonication in purified Millipore water (resistivity 18 M $\Omega$ .cm), 1:1 water/ethanol mixture, chloroform and heptane, followed by piranha treatment (1/3 v/v of 30% H<sub>2</sub>O<sub>2</sub>/98% H<sub>2</sub>SO<sub>4</sub>) at 80°C and exposure to UV under oxygen atmosphere for 30 min. The cleaned wafers were rinsed with purified water, dried with nitrogen and silanized in a 2 mM solution of octadecyltrichlorosilane (OTS) in heptane for 1 day. The wafers were then sonicated in chloroform and purified water and dried with nitrogen before UV/ozone treatment.

The silanized wafers were then exposed to UV light (185 and 254 nm) in an oxygen filled chamber at a distance of 4 cm from the lamp, for specific time periods, rinsed with purified water and chloroform and dried with nitrogen.

The OTS layers were first characterized using x-ray reflectivity using a Siemens powder diffractometer D5000 operated with a home-made software. The Cu  $K_{\alpha}$  is first collimated using 50- $\mu\text{m}$  slits. A graphite monochromator is placed after the sample in front of the NaI scintillator detector. The home-made software allows one to record rocking curves at each point of the reflectivity curve in order to subtract the background. Best fit of the reflectivity curve to a model describing the OTS layer as a single slab of constant electron density gives a substrate roughness of 0.4 nm, an OTS layer thickness of 2.45 nm and an OTS layer -air roughness of 0.65 nm in good agreement with Ref.<sup>13</sup> After 6 min UV ozone treatment, the thickness of the OTS layer decreases to 2.27 nm whereas its roughness increases to 0.785 nm, indicating changes in the top surface structure and composition. Attempts to add a specific surface layer to the model did not lead to significantly better fits.

The surface energy of the native and oxidized silane layers were also carefully characterized. The surface energy of solid surfaces is usually characterized through so-called Zisman plots which consist in plotting the cosine of the contact angle  $\theta$  of an homologous series of liquids as a function of the liquid surface tension  $\gamma$  of the liquid (Figure 2(a)).<sup>14,15</sup> The intercept at  $\cos \theta=1$  gives the critical surface tension of the surface  $\gamma_c$  which indicates whether a given liquid will wet ( $\gamma < \gamma_c$ ) or not ( $\gamma > \gamma_c$ ) the substrate. In principle, non-polar homologous liquids like alkanes should be used, but in practice this also works very well even with water.<sup>16</sup> From fitting the Zisman plots for tetradecane, hexadecane, squalane, bicyclohexyl, diiodomethane and purified water (Figure 2(a)), we obtain the critical surface tensions shown in Figure 2(b). The critical surface energies range from 19.6 mN/m for the native surface layer in good agreement with literature,<sup>17</sup> to 27.7 mN/m after 8 minutes UV irradiation, demonstrating that our method allows a very precise control of the surface energy, down to a fraction of a mN/m. In order to characterize the surface independently of our irradiation time (a parameter which may vary from an apparatus to another), we report in Figure 1(b) the critical surface tension as a function of the water contact angle. This parameter is very sensitive to the oxidation state of the surface. A very smooth and linear variation is then obtained over a range of angles

very similar to the one found by Han et al.<sup>6</sup>

Diblock copolymers of PS<sub>52K</sub>-*b*-PMMA<sub>52K</sub> (PDI: 1.09) of symmetric composition and PS<sub>46K</sub>-*b*-PMMA<sub>21K</sub> (PDI: 1.09) of asymmetric composition were purchased from *Polymer Source Inc.* PS<sub>52K</sub>-*b*-PMMA<sub>52K</sub> exhibits a lamellar phase of period  $L_0 = 49\text{nm}$  in the bulk whereas PS<sub>46K</sub>-*b*-PMMA<sub>21K</sub> exhibits a phase of PMMA cylinders (of about 36 nm for the center to center spacing) in PS. 1 wt% solutions of PS<sub>52K</sub>-*b*-PMMA<sub>52K</sub> and PS<sub>46K</sub>-*b*-PMMA<sub>21K</sub> in toluene were spin-coated onto silanized silicon wafers treated with UV/ozone at 2000 and 2500 rpm to produce copolymer films with thicknesses *ca.* 34 nm and 31 nm, respectively. Subsequently, the samples were annealed in a vacuum oven of pressure less than 3 kPa at 170 °C for 1 day.

Atomic force microscopy (AFM, Digital Instruments, Nanoscope V) was employed in tapping mode for imaging PS-PMMA films at room temperature. Phase images allow one to easily distinguish PS (dark) from PMMA (bright) domains.<sup>18</sup> After spin coating, due to low surface energies, no copolymer was observed on non-treated ( $\gamma_C = 19.6\text{mN/m}$ ) and 3-min UV/ozone treated ( $\gamma_C = 21.6\text{mN/m}$ ) samples. For the samples with water contact angles of 87° and 84°, dewetting can be observed under optical microscopy and AFM (inserts of ??(a,f)). As shown in ??(a-e) perpendicular orientation of the lamellar phase of the PS<sub>52K</sub>-*b*-PMMA<sub>52K</sub> copolymer is obtained on the samples with  $\gamma_C$  from 23.9 to 25.7 mN/m. Its period is *ca.* 50 nm as expected from bulk studies. ??(f-j) show the different morphologies obtained after UV/ozone treatment for the PS<sub>46K</sub>-*b*-PMMA<sub>21K</sub> copolymer films. First, on the sample with  $\gamma_C = 22.7\text{mN/m}$ , dewetting of copolymer is observed after annealing (??(f)). Perfect perpendicular orientation of the cylinders is obtained after 5 min UV/ozone treatment (??(g),  $\gamma_C=24.6\text{ mN/m}$ ). From the FFT of AFM images, the average distance between them is 33 nm. After 6 min (??(h),  $\gamma_C=25.8\text{mN/m}$ ), the phase contrast is obviously much reduced and the orientation is lost. After 7 min treatment, elongated structures are observed (??(i),  $\gamma_C=26.8\text{mN/m}$ ). The structure gives a spacing of 39 nm, which is close to the value of  $33\text{nm} \times 2/\sqrt{3}$ . This indicates that they should be the same cylindrical structure observed on 5-min treated sample but lie flat on the surface. Finally, after 8 and 9 min treatment (??(j),  $\gamma_C=27.7\text{ mN/m}$ ) this orientation is lost again.

In this paper, we have demonstrated that UV/ozone oxidation of OTS layers provides a simple and versatile way of controlling the orientation of block copolymers through a precise control of the surface energy. As already noticed in the literature, the window for the perpendicular orientation of the lamellar phase is wider than for the cylindrical phase.<sup>5</sup> According to literature, the surface tensions of PS and PMMA at 170°C are  $\gamma_{\text{PS}} \approx 29.7 - 29.9 \text{ mN/m}$   $\gamma_{\text{PMMA}} \approx 29.9 - 31 \text{ mN/m}$  respectively.<sup>2,19,20</sup> If we assume that the neutral surface would have a surface energy of  $\approx 29.9 \text{ mN/m}$ , then this would be  $\approx 5 \text{ mN/m}$  more than the corresponding critical surface tension of  $24.5 \text{ mN/m}$ . According to,<sup>19</sup> there is a good agreement between surface energy and critical surface tension for PMMA but a large discrepancy for PS and polyethylene, for which the critical surface tension is also found to be  $\approx 4 \text{ mN/m}$  smaller than the 20°C surface energy. Whereas the OTS chains probably expose more methyl groups to the surface (which would also explain the lower critical surface tension with respect to polyethylene surface tension), this shows that such a difference is not unrealistic.

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## References

- (1) Kellogg, G. J.; Walton, D. G.; Mayes, A. M.; Lambooy, P.; Russell, T. P.; Gallagher, P. D.; Satija, S. *Physical Review Letters* **1996**, *76*, 2503–2506.
- (2) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. J. *Science* **1997**, *275*, 1458–1460.
- (3) Huang, E.; Russell, T. P.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Hawker, C. J.; Mays, J. W. *Macromolecules* **1998**, *31*, 7641–7650.
- (4) Ryu, D. Y.; Wang, J.-Y.; Lavery, K. A.; Drockenmuller, E.; Satija, S. K.; Hawker, C. J.; Russell, T. P. *Macromolecules* **2007**, *40*, 4296–4300.

- (5) Ham, S.; Shin, C.; Kim, E.; Ryu, D. Y.; Jeong, U.; Russell, T. P.; Hawker, C. J. *Macromolecules* **2008**, *41*, 6431–6437.
- (6) Han, E.; Stuen, K. O.; La, Y.-H.; Nealey, P. F.; Gopalan, P. *Macromolecules* **2008**, *41*, 9090–9097.
- (7) Park, D.-H. *Nanotechnology* **2007**, *18*, 355304.
- (8) Niemz, A.; Bandyopadhyay, K.; Tan, E.; Cha, K.; Baker, S. M. *Langmuir* **2006**, *22*, 11092–11096.
- (9) Kim, T. K.; Yang, X. M.; Peters, R. D.; Sohn, B. H.; Nealey, P. F. *Journal of Physical Chemistry B* **2000**, *104*, 7403–7410.
- (10) Peters, R. D.; Yang, X. M.; Kim, T. K.; Sohn, B. H.; Nealey, P. F. *Langmuir* **2000**, *16*, 4625–4631.
- (11) Delorme, N.; Bardeau, J.-F.; Bulou, A.; Poncin-Epaillard, F. *Thin Solid Films* **2006**, *496*, 612 – 618, .
- (12) Smith, A. P.; Sehgal, A.; Douglas, J. F.; Karim, A.; Amis, E. J. *Macromolecular Rapid Communications* **2003**, *24*, 131–135.
- (13) Tidswell, I. M.; Ocko, B. M.; Pershan, P. S.; Wasserman, S. R.; Whitesides, G. M.; Axe, J. D. *Phys. Rev. B* **1990**, *41*, 1111–1128.
- (14) de Gennes, P. G. *Rev. Mod. Phys.* **1985**, *57*, 827–863.
- (15) Zisman, W. In *Contact Angle, Wettability and Adhesion, Advances in Chemistry Series*; American Chemical Society, Washington D.C., 1964; p 1.
- (16) van Giessen, A.; Bukman, D.; Widom, B. *Journal of Colloid and Interface Science* **1997**, *192*, 257–265.
- (17) Brzoska, J. B.; Ben Azouz, I.; Rondelez, F. *Langmuir* **1994**, *10*, 4367–4373.
- (18) Magonov, S.; Reneker, D. *Annual Review of Materials Science* **1997**, *27*, 175–222.

(19) Wu, S. *J. Phys. Chem.* **1970**, 74, 632–638.

(20) Chee, K. *Journal of Applied Polymer Science* **1998**, 70, 697–703.

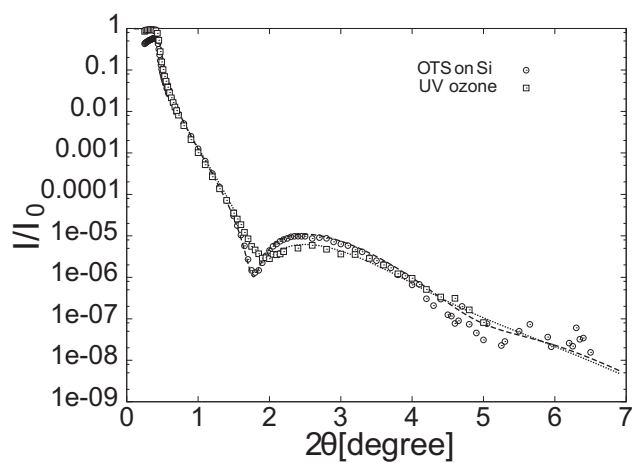


Figure 1: Reflectivity results of a typical silane layer (circle) and a 6-min UV ozone treated silane layer with the calculated curves (dash line and dot line respectively)



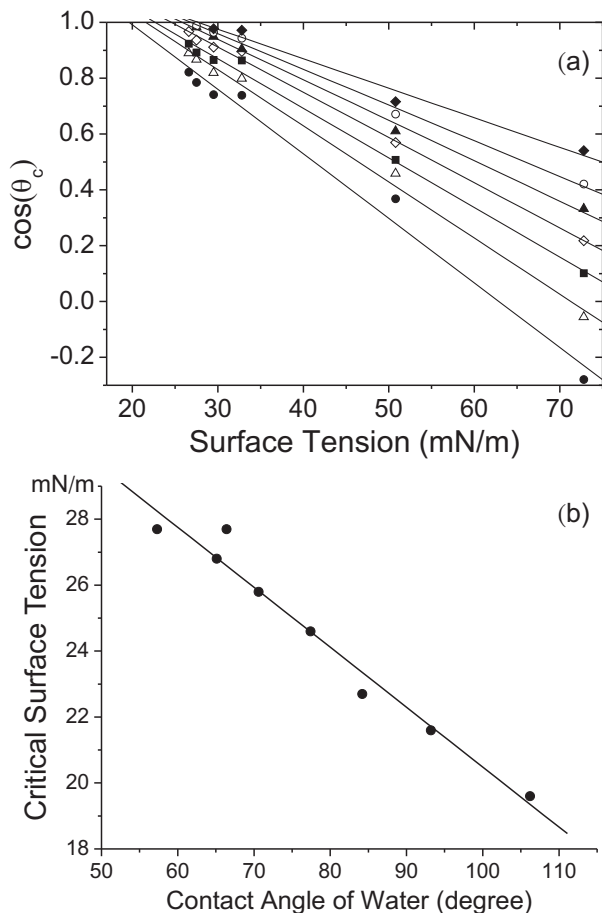


Figure 2: (a) Zisman plots, cosine of the contact angle  $\cos \theta_c$  as a function of the surface tension for tetradecane, hexadecane, squalane, bicyclohexyl, diiodomethane and purified water for silanated wafers treated with different UV/ozone time periods: native wafer (filled circles), 3 min (open triangles), 4 min (filled squares), 5 min (open diamonds), 6 min (filled triangles), 7 min (open circles), 9 min (filled diamonds). (b) Critical surface tensions as determined by the intercepts of the curves as a function of water contact angle chosen as a sensitive characteristic parameter of the surface.

Table 1: Results of contact angles, critical surface energies and the phases observed in AFM images.

Sample	$\theta_{C,water}(^{\circ})^a$	$\gamma_C(mN/m)^b$	description <sup>c</sup>
C1	84	22.7	
C2	77	24.6	$C_{\perp}$
C3	71	25.8	
C4	65	26.8	$C_{//}$
C5	57	27.7	
L1	87	22.7 <sup>d</sup>	dewetting
L2	80	23.9 <sup>d</sup>	$L_{//}$
L3	77	24.5 <sup>d</sup>	$L_{//}$
L4	70	25.7 <sup>d</sup>	$L_{//}$
L5	62	27.1 <sup>d</sup>	dewetting

<sup>a</sup>Contact angles of water in degrees.

<sup>b</sup>Critical surface energy values in mN/m.

<sup>c</sup>The phases or morphology observed in AFM images.

<sup>d</sup>Values calculated from linear interpolation of  $\theta_{C,water}$ .

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